Design strategies to minimize the radiative efficiency of global warming molecules

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A strategy is devised to screen molecules based on their radiative efficiency. The methodology should be useful as one additional constraint when determining the best molecule to use for an industrial application. The strategy is based on the results of a recent study where we examined molecular properties of global warming molecules using ab initio electronic structure methods to determine which fundamental molecular properties are important in assessing the radiative efficiency of a molecule. Six classes of perfluorinated compounds are investigated. For similar numbers of fluorine atoms, their absorption of radiation in the IR window decreases according to perfluoroethers > perfluorothioethers≈ sulfur/carbon compounds > perfluorocarbons > perfluoroolefins > carbon/nitrogen compounds. Perfluoroethers and hydrofluorethers are shown to possess a large absorption in the IR window due to (*i*) the C—O bonds are very polar, (*ii*) the C-O stretches fall within the IR window and have large IR intensity due to their polarity, and (*iii*) the IR intensity for C-F stretches in which the fluorine atom is bonded to the carbon that is bonded to the oxygen atom is enhanced due to a larger C—F bond polarity. Lengthening the carbon chain leads to a larger overall absorption in the IR window, though the IR intensity per bond is smaller. Finally, for a class of partially fluorinated compounds with a set number of electronegative atoms, the overall absorption in the IR window can vary significantly, as much as a factor of 2, depending on how the fluorine atoms are distributed within the molecule.

quantum chemistry calculations | climate change | fluorocarbons | infrared absorption | vibrational frequency

It has become increasingly clear that molecules other than CO_2 have the capability to significantly impact the global climate through global warming (1–4). Hansen et al. argued in 2000 that global warming in recent decades has been driven by green house gases (GHGs) other than CO_2, such as chlorofluorocarbons (CFCs), methane, and nitrous oxide (1). In 2007, Shine and Sturges quantified this further by arguing that about 40% of the heat trapped by anthropogenic GHGs is due to non-CO_2 gases and that the primary source was methane (2). However, in 2009 Velders et al. reported the results of model calculations suggesting that the radiative forcing due to hydrofluorocarbons (HFCs) will increase significantly in the coming decades as they are increasingly used to replace hydrochlorofluorocarbons (HCFCs) and CFCs, and demand for their use increases (3). One example of a class of molecule that can impact global climate change was provided in 2004 when Bera et al. predicted that the cyclic perfluorocarbon radicals and anions possess very large total IR intensities and a majority of the infrared absorption falls in the atmospheric infrared window (4).

The radiative forcing contribution due to halocarbons as a class is third only to carbon dioxide and methane according to the Intergovernmental Panel on Climate Change (IPCC) 2007 assessment report (5). Perfluorocarbons (PFCs) and HFCs are used heavily in the air conditioning, carpeting, and electronics industries. They are also used in atmospheric tracer studies, underground leak detection, and in some medical applications (6, 7). HFCs and PFCs, being potent greenhouse gasses, absorb and trap IR radiation rather effectively. In addition, these compounds do not react easily with hydroxyl radicals and they are generally hydrophobic, so they do not dissolve into atmospheric aerosols and clouds. Thus their atmospheric destruction rate is slow, which means HFCs and PFCs can have very long atmospheric lifetimes, of the order of thousands of years for PFCs. To summarize, both the modeling studies mentioned above and the IPCC 2007 report show that where global warming and global climate change is concerned, it is important to consider the impact from molecules other than just CO_2 and methane.

Recently, we reported a study aimed at understanding the fundamental molecular properties that are inherently important for a molecule's radiative efficiency (8), which directly impacts the global warming potential (GWP) for a given molecule (9). As discussed in the IPCC 2007 report, the GWP of a molecule is defined as the time-integrated global mean radiative forcing of a pulse emission of 1 kg of the molecule relative to that of 1 kg of a reference gas, usually taken to be CO_2 (5). The report further shows that the radiative forcing of a molecule is basically a product of its radiative efficiency and its atmospheric abundance. Our recent study has focused on a molecule's radiative efficiency within the atmospheric window region of the IR spectrum, which can be thought of as a molecule's inherent ability to absorb radiation in the atmospheric window. Our study demonstrated that a large radiative efficiency results for molecules, particularly carbon compounds, that contain several polar bonds, such as C—F bonds, and that this effect is enhanced nonlinearly when more and more electronegative elements are bonded to a single carbon. We showed that this results in the carbon atom becoming increasingly positive, while the fluorine atoms all retain about the same degree of negative character, resulting in more polar C—F bonds. Further, our study showed that the greater polarity in the bonds led to larger dipole derivatives in the C-F stretching vibrational modes, which leads to a quadratic increase in the IR intensity.

Other recent studies have reported on aspects of a molecule's structure in relation to its radiative efficiency (10, 11). Blowers et al. (10) have examined the GWPs of hydrofluoroethers (HFEs) and noted that their radiative forcing values increase with an increasing number of C—F bonds, but they assert a linear relationship between the radiative forcing and the number of C—F bonds, rather than the more complicated, nonlinear relationship found in our study. More recently, Young et al. (11) have derived a structure activity relationship for fluoriniated ethers as related to their radiative efficiency. While they show that there is indeed an influence on a molecule's radiative efficiency with respect to whether a CF_3 group is bonded to the ether oxygen atom or

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whether it is more removed from the ether oxygen, for example, their study misses the underlying fundamental molecular properties responsible for radiative efficiency. Both of these recent studies are useful, but they are limited in their predictive capability, and especially in transferability of their conclusions and suggestions to other classes of compounds, which is simply because neither of these studies identified the fundamental molecular properties involved in determining a molecule's radiative efficiency and how these might be used to identify strategies for minimizing a molecule's radiative efficiency.

The purpose of the present study is to demonstrate that the concepts developed in our recent study may be used in design strategies for deciding which industrial molecules will have the least impact on climate change, at least as far as radiative efficiency, and thus GWPs, is concerned. It is expected that the strategies we develop here could be used by industrial chemists as one additional constraint in their attempts to optimize molecules and processes used in their particular application.

Results and Discussion

Contained in Table 1 are data obtained from our ab initio calculations for perfluorinated species of different classes of compounds including CF_3CF_3, CF_3OCF_3, CF_3SCF_3, CF_3NF_2, SF_5CF_3, and CF_3CFCF_2. The choice of these classes of compounds for inclusion in the present study is based on the direction industry has moved over the last 10–20 years in replacing HCFCs and CFCs. The main criteria that industry has used in the selection of these classes of compounds (whether perfluorinated or partially fluorinated) have been based on thermophysical properties, flammability, and ease of degradation in the atmosphere. In other words, radiative efficiency was not considered, even though the radiative efficiency of some of these compounds can be as much as 100 times greater than that of CO_2 on a per molecule basis (5, 8). Additionally, many of the compounds from the different classes have been studied only in the laboratory to examine thermophysical properties, ease of degradation, and degradation products. In situ measurements have not been made except for HFC-134a (CF_3CH_2F) and HFC-152a (CH_3CHF_2), which show accumulation in the atmosphere. For example, HFC-134a was almost undetectable before 1990; however, since then, the global average concentration has risen significantly to 35 ± 0.73 parts per trillion (ppt). The concentration of HFC-152a has risen steadily to 3.9 ± 0.11 ppt (5).

The data in Table 1 include bond dipoles (BD), dipole derivatives (DD), harmonic vibrational frequencies, IR intensities, the total summed IR intensities, and the summed IR intensities that appear in the infrared window (IRW). Earth's atmosphere is relatively opaque below 800 cm^{-1} and above 1,400 cm^{-1}, leading to an atmospheric window between about 800 and 1,400 cm^{-1} through which blackbody radiation emitted by the Earth is lost and a temperature balance is achieved. There is no unique definition of the "atmospheric window," and some researchers have defined the wavelength range from 8.5 to 11 μm (for example, see refs. 12 and 13, and references therein). However, for purposes of this study, we use a broad range and define the IRW to be 800 to 1,400 cm^{-1} (about 8 to 13 μm).

The data in Table 1 show in general which classes of compounds can be expected to exhibit a larger radiative efficiency due to their fundamental molecular properties. Because they are all perfluorinated compounds, they all exhibit large radiative efficiencies, but they are not all equal. In particular, the perfluorinated ether, CF_3OCF_3, possesses a 78% increase in IR absorption in the IRW compared to the perfluorocarbon CF_3CF_3. The fact that perfluorinated ethers possess a larger radiative efficiency compared to the analogous perfluorocarbon has been known

Table 1. BD and DD (both atomic units), harmonic vibrational frequencies (cm^{-1}), IR intensities ($km\,mol^{-1}$), total IR intensity, and IR intensity within the IR window for six perfluorinated molecules representative of six classes of global warming molecules

	CF_3CF_3		CF_3OCF_3		CF_3SCF_3		CF_3NF_2		SF_5CF_3		CF_3CFCF_2*	
BD	CF 2.56		CO 3.20	CF 3.03	CS 2.74	CF 2.23	CF 2.33	NF 0.66	CF 3.65	SF 2.46	CC 1.37	CF 1.74
BD											CF 0.83	CF 2.05
DD	CF 4.60	CC 0.0	CO 4.53	CF 4.61	CS 1.13	CF 4.89	CF 4.53	NF 3.78	CF 4.76	SF 4.68	CC 1.45	CF 5.16
DD							CN 1.63		CS 0.80		CF 4.63	CF 4.72
	Freq	Inten	Freq	Inten	Freq	Inten	Freq	Inten	Freq	Inten	Freq	Inten
	71	0.0	52	0.0	29	0.0	106	0.0	9	0.1	47	0.1
	218	3.2	96	0.1	79	0.1	245	2.3	211	0.8	134	0.5
	218	3.2	177	0.5	135	1.2	276	1.6	217	0.8	141	1.7
	353	0.0	344	0.0	285	0.9	376	0.2	302	0.4	251	1.3
	379	0.0	356	0.3	288	0.0	430	0.2	313	1.1	282	2.8
	379	0.0	367	0.0	311	0.0	521	4.5	327	0.8	357	0.6
	518	5.2	465	0.4	365	0.1	575	4.7	352	0.2	377	1.5
	518	5.2	528	3.3	485	9.7	601	4.5	406	2.1	436	3.1
	618	0.0	569	3.5	490	6.9	722	25.1	407	1.8	500	2.6
	618	0.0	586	0.0	543	1.9	862	7.6	470	0.0	558	0.6
	710	38.0	655	9.0	544	0.0	967	98.3	536	12.5	598	0.5
	809	0.0	690	32.7	546	2.3	1,030	86.8	537	12.9	644	3.1
	1,123	301.7	745	2.8	595	6.1	1,267	199.4	573	1.4	656	15.4
	1,254	0.2	856	0.4	769	2.3	1,310	333.4	576	0.7	765	12.5
	1,254	0.4	972	93.4	770	23.8	1,311	344.5	590	55.3	1,041	232.8
	1,271	613.3	1,205	434.3	1,105	496.8			610	0.1	1,192	336.1
	1,271	613.3	1,232	1.0	1,179	301.8			662	6.1	1,217	340.3
	1,468	0.0	1,264	753.7	1,183	3.9			751	110.0	1,253	18.6
			1,282	722.3	1,191	33.6			871	345.5	1,370	256.8
			1,301	114.0	1,214	586.6			890	361.0	1,432	236.6
			1,349	596.0	1,247	489.3			890	361.4	1,842	149.1
									1,174	135.0		
									1,283	306.9		
									1,288	313.1		
	Total	1,583.4		2,767.7		1,967.3		1,113.1		2,030.0		1,616.6
	IRW	1,528.6		2,715.1		1,912.0		1,070.0		1,822.9		1,421.2

Computed at the MP2/DZP++ level of theory—see the text for details.

*Top left: CC single bond; top right: CF of the end CF_2; bottom left: middle CF; bottom right: CF of the CF_3 group.

(10, 11, 14, 15), but the data in Table 1 show that this is for three main reasons: first, the C—F bond dipole is larger for CF_3OCF_3 compared to CF_3CF_3, leading to larger IR intensities for the C-F stretches; second, the C—O bond dipole is very large, leading to large IR intensities for the C-O stretches, which fall into the IR window region (there is significant mixing between the C-O and C-F stretches, but a total energy distribution analysis shows that the bands at 1,205 and 1,301 cm^{-1} are mainly C-O stretches; see the *SI Appendix*); and third, because of the reduced symmetry in CF_3OCF_3 compared to CF_3CF_3, there are four C-F stretching modes that have significant intensity, though the fourth-most intense mode at 972 cm^{-1} has an IR intensity of only 94 km mol^{-1}, compared with 755 km mol^{-1} for the most intense C-F stretch (note that this third component, symmetry, will not necessarily be present in larger perfluorcarbons where the molecular symmetry is lowered relative to CF_3CF_3). Hence perfluorinated ethers possess enhanced IR intensities for the C-F stretches relative to perfluorocarbons, and they add two more C-O stretching modes with large IR intensities in the IRW.

The two sulfur-containing compounds included in Table 1, CF_3SCF_3 and SF_5CF_3, also exhibit total absorptions in the IRW that are larger than the perfluorocarbon CF_3CF_3. For the perfluorothioether CF_3SCF_3, this is largely due to factor three noted above, namely that there are now four C-F stretching modes with significant IR intensity, rather than just three for CF_3CF_3. The C—F bond dipole is somewhat smaller in CF_3SCF_3 compared to CF_3CF_3, and the C-S stretches either fall out of the IRW (490 cm^{-1}) or do not possess a very large IR intensity (24 km mol^{-1} for the 770 cm^{-1} band). SF_5CF_3 contains more fluorine atoms than the other perfluoro compounds in Table 1 and hence more X-F stretching modes. As it turns out, only six of the X-F stretching modes fall within the IRW (the three C-F stretches and only three of the S-F stretches), but all six modes have an appreciable IR intensity ranging from 110 to 362 km mol^{-1}, whereas the two S-F stretching modes that fall below the IRW (at 610 and 662 cm^{-1}) both have rather small IR intensities. In addition, the C-S stretch is well below the IRW (313 cm^{-1}) and also possesses a small IR intensity.

CF_3CFCF_2 is a perfluoroolefin, so it possesses a C=C double bond and is one of the newer class of molecules to be considered as an HCFC or CFC replacement. Having a C=C double bond means that the molecule is more reactive, leading to a smaller atmospheric lifetime, but it also possesses fewer C—F bonds, leading to a lower radiative efficiency. In Table 1, CF_3CFCF_2 is shown to have a smaller radiative efficiency relative to the perfluorocarbon CF_3CF_3, 1,421 km mol^{-1} compared to 1,529 km mol^{-1}, even though both molecules contain six C—F bonds. Moreover, we included a C-C stretching band with a large IR intensity at 1,428 cm^{-1} for CF_3CFCF_2, since with anharmonicity the band center would probably fall near 1,400 cm^{-1} and thus will be at least partially in the IRW. For all of the other perfluoro compounds included in Table 1, this was not an issue because any bands that fall just below 800 cm^{-1} or just above 1,400 cm^{-1} have very small IR intensities. The bond dipole data for CF_3CFCF_2 show that the average C—F bond dipole, 1.74 a.u., is quite a bit smaller than the value for CF_3CF_3, 2.56 a.u., which explains why CF_3CFCF_2 has a lower overall absorption in the IRW window even with inclusion of the C-C stretch.

CF_3NF_2 is the last perfluoro compound to be discussed from Table 1. This molecule has a significantly lower IR absorption in the IRW compared to CF_3CF_3—a 30% reduction. This occurs for two reasons: the N—F bond dipole is much smaller than the C-F value found in either molecule, and thus the two N-F stretching modes (967 and 1,030 cm^{-1}) possess small IR intensities relative to the average C-F mode, and the C—F bond dipole is smaller in CF_3NF_2 compared to CF_3CF_3 leading to a smaller average IR intensity for the C-F modes (862, 1,310, and 1,311 cm^{-1}). It may appear that another factor is the smaller number of X—F bonds in CF_3NF_2 relative to CF_3CF_3, but the C-N stretch (1,267 cm^{-1}) occurs in the IRW, and whereas it has a significant IR intensity (200 km mol^{-1}), it is quite a bit less than the average of the two C-O stretches in CF_3OCF_3 (274 km mol^{-1}). To summarize, CF_3NF_2 exhibits a smaller absorption in the IRW compared to CF_3CF_3 because the N—F and C—F bond dipoles in the former are smaller than the C—F bond dipole in the latter, leading to smaller IR intensities for the stretching modes that appear in the IRW.

A final comment regarding the bond dipole and dipole derivative values reported in Table 1: Bond dipoles are not directly connected to an experimental observable, and thus by necessity their evaluation is performed using a technique that is qualitative and not unique. Dipole derivative values may be connected to an experimental observable (the IR intensity), but only for the actual fundamental vibrational modes and not necessarily for a simple internal coordinate dipole derivative. In the fundamental vibrational modes, the C—F bond stretches may cancel the molecular dipole or they may enhance one another, which is why some of the C-F stretching modes have a small IR intensity and others are very large. The discussion above shows that several factors contribute to a molecule's overall absorption in the IRW, but that an important one is the polarity of the bonds whose stretching modes will appear in the IRW.

Contained in Table 2 are perfluorinated species from the same class of compounds investigated in Table 1 (except for the perfluoroolefin class), but with longer carbon chains. The data contained in Table 2 include the molecule's total IR intensity, the IR intensity in the IRW, the percent that the latter is of the former, and the IR intensity (in the IRW) per bond stretch that appears in the IRW. For example, for CF_3CF_3, there are six C—F bonds that fall in the IRW (the C-C stretch does not fall in the IRW), and the IR intensity in the IRW is 1,528.9 km mol^{-1}, so the IR intensity per bond is $1{,}528.9/6 = 254.8$ km mol^{-1}. Note that labeling of the vibrational modes is accomplished using a total energy distribution (TED) analysis and should be considered qualitative since in the larger molecules there is considerable mixing, as is usual. The TED analyses are included in the *SI Appendix*, along with the optimized molecular geometries, harmonic vibrational frequencies, and the IR intensities. Examination of the perfluorocarbon series of molecules shows that the IR absorption in the IRW increases as the chain becomes longer, but that the percent of the IR intensity in the IRW decreases, and more importantly the IR intensity per bond stretch decreases. We note, however, that as the carbon chain becomes longer for these perfluorinated species, some of the C-C stretch vibrational modes fall into the IR window, which further reduces the IR intensity per bond stretch because on average the IR intensity for the C-C stretches is smaller than for the C-F stretches.

For most of the classes of compounds investigated here, examination of Table 2 shows that this trend is generally the same: As the carbon chain increases in length, the total IR absorption, as well as the absorption in the IRW increases, but the percentage of the molecule's IR intensity in the IRW decreases slightly, while the IR intensity per bond also decreases. The only exception to this trend is on going from NF_3 to CF_3NF_2, where the IR intensity per bond increases slightly, which is due to the previously noted fact that the N—F bonds are less polar than C—F bonds and thus possesses a smaller IR intensity. However, on going to longer carbon chains such as $CF_3CF_2NF_2$, the trend is reestablished and the IR intensity per bond decreases. The results in Table 2 show that while longer carbon chain perfluorinated compounds possess a smaller IR intensity per bond in the IRW, this is advantageous only if the longer chain means fewer molecules are needed in an industrial process or application since the IR absorption appearing in the IRW on a per molecule basis increases relative to the shorter carbon chain species.

One of the important conclusions to come out of our previous study was the enhanced effect multiple fluorine atoms bonded to

Table 2. Total IR intensity (km mol^{-1}), IR intensity in the IRW, percent of IR intensity in the IRW, and IR intensity per stretching vibration within the IRW for perfluorinated molecules representative of five classes of global warming molecules

	Formula	Total IR intensity, km mol^{-1}	Intensity in IRW, km mol^{-1}	% in IRW	Intensity per bond
CFC-116	CF_3CF_3	1,583.7	1,528.9	96.5	254.8
PFC-218	$CF_3CF_2CF_3$	1,883.0	1,788.9	95.0	223.6
PFC-3-1-10	$CF_3CF_2CF_2CF_3$	2,165.5	2,025.8	93.5	184.2
	CF_3OCF_3	2,767.1	2,714.6	98.1	339.3
	$CF_3CF_2OCF_3$	2,995.3	2,894.4	96.6	289.4
	$CF_3CF_2OCF_2CF_3$	3,197.2	3,043.1	95.2	253.6
	CF_3SCF_3	1,967.2	1,912.0	97.2	318.7
	$CF_3CF_2SCF_3$	2,242.3	2,149.7	95.9	238.9
	$CF_3CF_2SCF_2CF_3$	2,466.9	2,338.0	94.8	194.8
	SF_6	1,485.0	1,392.9	93.8	464.3
	SF_5CF_3	2,029.5	1,823.0	89.8	303.8
	$SF_5CF_2CF_3$	2,313.8	2,099.5	90.7	233.3
	NF_3	519.9	516.2	99.3	172.1
	CF_3NF_2	1,112.8	1,069.9	96.1	178.3
	$CF_3CF_2NF_2$	1,369.6	1,264.6	92.3	158.1

Computed at the MP2/DZP++ level of theory—see the text for details.

the same carbon atom have on the C-F stretch IR intensities. Specifically, we found that each additional fluorine atom caused the central carbon atom to be more positive, resulting in a larger bond dipole for all C—F bonds, and hence an enhanced IR intensity for all C—F bonds. This result suggests that for partially fluorinated compounds, it is important to consider not just how many fluorine atoms the compound contains, but also their placement in the molecule, and in particular one should try to minimize the number of fluorine atoms bonded to a specific carbon, sulfur, or nitrogen central atom. Contained in Table 3, then are results from ab initio calculations for various partially fluorinated molecules from the two classes of compounds that are most popular for industrial use—namely HFCs and HFEs, and for a set of hydrofluoroolefins (HFOs) in which there are four fluorine atoms. Table 3 is organized according to the number of X—F bonds contained in the molecule, and the data presented include the total IR intensity, the IR intensity within the IRW, and the percent of the IR intensity contained in the IRW. We have included some compounds with only one fluorine atom in Table 3 for completeness, but most industrial applications will use molecules with a larger fluorination. Examination of the data presented in Table 3 for the molecules with two fluorine atoms shows that, not surprisingly, the two HFEs exhibit a significantly larger IR absorption in the IRW relative to the two HFCs. Further, the IR absorption in the IRW is larger when the two fluorine atoms are bonded to the same carbon atom, consistent with our earlier study, although the effect is larger for the CH_3CHF_2/CH_2FCH_2F pair compared to the CH_3OCHF_2/CH_2FOCH_2F pair.

Examination of the data for the compounds with three fluorine atoms again shows a sharp contrast between the HFCs and the HFEs, although there is now a much larger range for the HFEs due to the fact that longer chains have been included, yielding more possibilities for distributing the fluorine atoms around the molecule. Indeed, the IR intensity in the IRW for the HFEs ranges from 805 km mol^{-1} ($CH_3OCHFCHF_2$) to 1,565 km mol^{-1} ($CF_3OCH_2CH_3$). When the fluorine atoms are more distributed around the HFE, the C—F and C—O bond dipoles are smaller due to a smaller positive charge on the carbon atoms, and this leads to a smaller IR intensity in the IRW. This is demonstrated by the fact that the two HFEs with the largest IR intensity in the IRW both have all three fluorine atoms bonded to the same carbon atom that is also bonded to the oxygen atom. A second group of HFEs (IR intensity in the IRW > 1,200 km mol^{-1}) have all three fluorine atoms bonded to carbons that are also bonded to the oxygen atom (but not the same carbon atom). The remaining five HFEs have at least one fluorine atom bonded to a carbon that is not bonded to the oxygen atom. In addition, a minor trend is seen by comparison of the $CH_3OCHFCHF_2/CH_2FOCH_2CHF_2$ and $CH_3OCF_2CH_2F/CHF_2OCH_2CH_2F$ pairs, which shows that in both cases the molecule with all the fluorine atoms on the longer carbon chain rather than the single carbon (also bonded to the oxygen) has a slightly lower IR intensity in the IRW (by about 100 km mol^{-1}). This shows that there is a delicate balance involving the positive charge over all the carbon atoms in the HFE, whether bonded to the ether oxygen or bonded to fluorine atom(s).

For the HFCs with three fluorine atoms the range of IR intensity within the IRW is smaller, going from 334 to 819 km mol^{-1}. We have included HFCs with up to three carbon atoms, and they basically fall into three categories based on their IR intensity in the IRW: Those with all three fluorine atoms on the same carbon possess an IR intensity in the IRW near 800 km mol^{-1}, whereas those with two fluorine atoms bonded to the same carbon (and the third bonded to a different carbon) yield an IR intensity in the IRW near 500 km mol^{-1}, whereas the one HFC with the three fluorine atoms bonded to different carbon atoms has an IR intensity in the IRW window of 334 km mol^{-1}. The results presented here for HFCs and HFEs with three fluorine atoms demonstrate the importance of spreading out the fluorine atoms in these compounds and not having them bonded to the same carbon, or in the case of the HFEs, not bonded to a carbon that is also bonded to the oxygen atom.

Examination of the data in Table 3 for the hydrofluoroolefins with four fluorine atoms is illuminating. The absorption in the IRW ranges from 624 km mol^{-1} for CHF_2CHCF_2 to 914 km mol^{-1} for CF_3CFCH_2, but similar to the situation for CF_3CFCF_2, there are bands with significant IR intensity either just above 1,400 cm^{-1} (CF_3CFCH_2) or just below 800 cm^{-1} (CH_2FCFCF_2 and CHF_2CHCF_2) for some of these compounds. For CF_3CFCH_2 there is a band at 1,418 cm^{-1} with an IR intensity of 130 km mol^{-1}. Including this band increases its total absorption in the IRW to 1,043 km mol^{-1}. Similarly, including the bands just below 800 cm^{-1} for CH_2FCFCF_2 and CHF_2CHCF_2 increases their total absorption in the IRW to 685 and 719 km mol^{-1}, respectively. It is also illuminating to note that three of the isomers, CF_3CHCHF, CH_2FCFCF_2, and CHF_2CHCF_2, possess significant IR intensity in the C=C double bond stretching mode (see the *SI Appendix*) while none of the others exhibit this property. This is important because the C=C double bond stretch occurs near 1,800 cm^{-1} for these molecules —well above the atmospheric IRW. Mulliken populations show that the C=C double bond is very polar in these compounds, consistent with the IR intensities. In fact, for two of the isomers, one of the olefin carbons exhibits a negative partial charge. Hence another feature of the hydrofluoroolefins is the ability to push

Table 3. Total IR intensity (km mol^{-1}), IR intensity in the IRW, and percent of IR intensity in the IRW, for various HFCs, HFEs, and HFOs

Industrial name	Formula	No. of F atoms	Integrated intensity, km mol^{-1}	Intensity in IRW, km mol^{-1}	%
HFC161	CH_3CH_2F	1	323.8	133.4	41.1
	CH_3OCH_2F	1	794.2	506.2	63.7
HFC152	CH_2FCH_2F	2	395.9	245.2	61.9
HFC152a	CH_3CHF_2	2	584.6	378.0	64.6
	CH_2FOCH_2F	2	1,010.2	806.3	79.8
	CH_3OCHF_2	2	1,182.6	831.4	70.3
HFC143	CH_2FCHF_2	3	637.9	481.2	75.4
HFC143a	CH_3CF_3	3	953.6	818.6	85.8
	$CH_3CH_2CF_3$	3	956.3	764.2	79.9
	$CH_3CHFCHF_2$	3	674.6	492.9	73.1
	$CH_3CF_2CH_2F$	3	656.1	492.3	75.0
	$CH_2FCH_2CHF_2$	3	728.3	475.7	65.3
	$CH_2FCHFCH_2F$	3	519.8	334.2	64.3
	CH_2FOCHF_2	3	1,408.6	1,226.0	87.0
HFE143a	CH_3OCF_3	3	1,585.0	1,450.1	91.4
HFE263fb2	$CH_3OCH_2CF_3$	3	1,309.7	1,029.6	78.6
	$CH_3OCHFCHF_2$	3	1,134.0	805.2	71.0
	$CH_2FOCHFCH_2F$	3	1,144.7	859.1	75.1
	$CH_3OCF_2CH_2F$	3	1,200.9	967.5	80.5
	$CH_2FOCF_2CH_3$	3	1,443.5	1,208.9	83.7
	$CHF_2OCHFCH_3$	3	1,583.6	1,278.7	80.7
	$CF_3OCH_2CH_3$	3	1,722.2	1,564.8	90.9
	$CH_2FOCH_2CHF_2$	3	1,221.9	917.6	75.1
	$CHF_2OCH_2CH_2F$	3	1,338.3	1,080.9	80.8
HFC134	CHF_2CHF_2	4	862.6	751.3	87.1
HFC134a	CH_2FCF_3	4	999.7	890.7	89.1
HFE134	CHF_2OCHF_2	4	2,132.9	1,571.0	73.6
HFO-1234yf	CF_3CFCH_2	4	1,182.9	913.5	77.2
	CF_3CHCHF	4	1,298.9	967.4	74.5
	CH_2FCFCF_2	4	928.7	638.4	68.7
	CHF_2CFCHF	4	891.1	717.4	80.5
	CHF_2CHCF_2	4	1,333.6	623.7	46.8
HFC125	CHF_2CF_3	5	1,225.0	1,123.1	91.6
HFC245ea	$CHF_2CHFCHF_2$	5	993.5	725.2	73.0
HFC245fa	$CHF_2CH_2CF_3$	5	1,376.8	1,025.6	74.5
HFC245eb	$CH_2FCHFCF_3$	5	1,108.3	902.8	81.5
HFC245ca	$CH_2FCF_2CHF_2$	5	926.6	775.1	83.6
HFC245cb	$CH_3CF_2CF_3$	5	1,224.1	1,090.4	89.1
HFE-125	CHF_2OCF_3	5	2,287.1	2,102.2	91.9
HFC236fa	$CF_3CH_2CF_3$	6	1,777.4	1,461.7	82.2
HFC236ea	CHF_2CHFCF_3	6	1,352.3	1,066.0	78.8
HFC236cb	$CH_2FCF_2CF_3$	6	1,280.4	1,121.5	87.5
	CF_3CFCF_2	6	1,616.6	1,421.2	87.9
	CF_3CF_3	6	1,583.7	1,528.9	96.5
PFE	CF_3OCF_3	6	2,767.1	2,714.6	98.1
HFE-236fa	$CF_3OCH_2CF_3$	6	2,428.8	2,276.0	93.7
	$CF_3CH_2OCH_2CF_3$	6	1,979.8	1,766.7	89.2
	$CHF_2CHFOCH_2CF_3$	6	1,857.9	1,570.2	84.5

Computed at the MP2/DZP++ level of theory—see the text for details.

some of the molecule's IR absorption outside the IRW, and this appears to be a function of the C=C double bond. Even so, the data for the hydrofluoroolefins presented in Table 3 show that all isomers are not equivalent, and it is important to spread out the fluorine atoms in order to yield a lower total absorption in the IRW.

There are some further examples presented in Table 3 of compounds with four, five, and six fluorine atoms, but due to the large number of possible compounds with ever-increasing carbon chain lengths, we have included only a subset of the possibilities. The series of HFEs with six fluorine atoms is interesting. CF_3OCF_3, not surprisingly, has the largest IR intensity in the IRW, 2,715 km mol^{-1}. The value for $CF_3OCH_2CF_3$ is reduced to 2,276 km mol^{-1}, and for $CF_3CH_2OCH_2CF_3$ it is reduced further to 1,767 km mol^{-1}. The latter molecule still has three electronegative atoms bonded to the two terminal carbon atoms, and only one electronegative atom (the oxygen) bonded to the two central carbons. Shifting one of the fluorine atoms from a terminal carbon to a central carbon, $CHF_2CHFOCH_2CF_3$, then reduces its IR intensity in the IRW to 1,570 km mol^{-1}, showing the importance of balancing the distribution of electronegative atoms. Examining the results for the remaining compounds shows that the basic conclusions remain the same: the more electronegative atoms (fluorine or oxygen) bonded to a carbon atom leads to a larger positive charge on the carbon atom, leading to more polar bonds, leading to larger IR intensities, and thus a larger molecular IR intensity in the IRW.

Conclusions

The radiative efficiency of six classes of perfluorinated molecules that each contain electronegative elements bonded to either a carbon, sulfur, or nitrogen atom have been studied using ab initio quantum chemistry methods as outlined in a recent study. The perfluoroether (PFE) class exhibits the largest absorption in the infrared window due to the addition of C-O stretches that occur in the infrared window and possess large IR intensities due to the polarity of the C—O bonds. In addition, the C—F bonds for any fluorine atoms bonded to the carbon that is also bonded

to the oxygen atom exhibit more polarity as a result and thus larger IR intensities for the C-F stretches that occur in the IRW. Perfluorinated thioether compounds and perfluorinated sulfur/carbon compounds (such as SF_5CF_3) show a somewhat larger absorption in the IRW than the corresponding PFCs. Perfluoroolefins exhibit a smaller absorption in the IRW relative to PFCs with the same number of fluorine atoms because on average the C—F bonds are less polar. Perfluorinated carbon/nitrogen compounds (such as CF_3NF_2) exhibit the smallest absorption of IR radiation in the IRW of the classes of perfluoro compounds studied here, and this is due to the fact that the N—F bonds are less polar than C—F bonds, and the C—N bond is less polar than the C—O bonds found in the PFE class of compounds. To summarize, the radiative efficiency decreases in the order PFE > perfluorinated thioethers≈ sulfur/carbon > PFC > perfluoroolefins > carbon/nitrogen for the six classes of perfluorinated compounds studied here.

As the molecular size of the perfluorinated compounds is increased by increasing the length of the carbon chain, the overall absorption in the IR window increases, though the absorption per bond stretch that occurs in the IRW decreases. This latter result, of course, is important only if use of the longer molecules means that fewer molecules are needed for whatever industrial process or application is being performed.

Finally, for partially fluorinated compounds, we have shown that it is important to minimize the number of electronegative elements bonded to the same carbon atom (or in the case of sulfur/carbon or carbon/nitrogen compounds, this should extend to the sulfur and nitrogen atoms), since as shown in our earlier study (8) this leads to a greater polarity in the C—F or C—O bonds, and hence larger IR intensities for the C-F and C-O stretches, which occur in the IR window. In the case of HFEs with three fluorine atoms, we show that judicious placement of the fluorine atoms can lead to an overall IR absorption in the IR window close to half what is found for the isomer where all the electronegative elements are bonded to the same carbon atom.

While previous studies also noted some of these structure relationships for HFEs (11, 15), our previous study (8) explained why this occurs using fundamental molecular properties, and thus we have extended these concepts to the other classes of compounds studied here. The current study is not meant to be an exhaustive survey of all molecules or even all classes of molecules that might be used in industrial applications, but rather it is meant to demonstrate how use of the concepts developed in our earlier study can be used to develop design strategies to engineer molecules with as small a radiative efficiency as possible. We note also that the strategies developed here should be considered one additional constraint in the development of molecules, with some others being efficacy for the particular industrial application being considered, toxicity, atmospheric lifetime, and atmospheric fate of derivative molecular species.

Theoretical Methods

Consistent with our first study, we have optimized molecular geometries using the restricted Hartree-Fock second-order Møller-Plesset perturbation theory (MP2), in conjunction with Dunning's (16, 17) double zeta plus polarization one-particle basis set that includes diffuse functions on all atoms (including hydrogen), denoted DZP + +. Exponents for the diffuse functions were determined using a standard approach (18) and are as follows: H s 0.04415; C s 0.04302, p 0.03629; O s 0.08227, p 0.06508; N s 0.06029, p 0.05148; F s 0.1049, p 0.0826; S s 0.1519, s 0.04267, p 0.5218, and p 0.1506. All electronic structure calculations were performed with the Q-Chem3.1 quantum chemistry program (19). Harmonic vibrational frequencies and IR intensities were computed at the same level of theory, i.e., MP2/DZP + +. The IR intensities were computed using the double harmonic approximation, meaning that an IR vibrational intensity is proportional to the square of the dipole derivative (20). Based on extensive comparisons with experimental data (for example, see ref. 21, and references therein), it is expected that the MP2/DZP + + IR intensities are between 5–20% too large. However, the error should be very consistent across the different fluorine compounds investigated in the current study because the electronic structure of the various compounds is similar, indicating that the relative error across the various compounds will be small. Consistent with our earlier study, in some cases the Cartesian dipole derivatives obtained at the MP2/DZP + + level of theory have been transformed into the simple internal coordinates for a given molecule in order to assess various molecular properties. For simplicity, the simple internal coordinates used are limited to the bond distances and angles of the molecules concerned. Intder2005,* a code for vibrational analysis and nonlinear transformations of quartic force fields (including property force fields), has been used to transform the Cartesian dipole derivatives into simple internal coordinate derivatives and to perform the TED analyses.

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1. Hansen J, Sato M, Ruedy R, Lacis A, Valder O (2000) Global warming in the twenty-first century: An alternative scenario. *Proc Natl Acad Sci USA* 97:9875–9880.
2. Shine KP, Sturges WT (2007) CO_2 is not the only gas. *Science* 315:1804–1805.
3. Velders GJM, Fahey DW, Daniel JS, McFarland M, Anderson SO (2009) The large contribution of projected HFC emissions of future climate forcing. *Proc Natl Acad Sci USA* 106:10949–10954.
4. Bera PP, Horny L, Schaefer HF (2004) Cyclic perfluorocarbon radicals and anions having high global warming potentials (GWPs): Structures, electron affinities, and vibrational frequencies. *J Am Chem Soc* 126:6692–6702.
5. Forster P, et al. (2007) *Climate Change 2007: The Physical Science Basis. Contribution of Working group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, eds S Solomon et al. (Cambridge Univ Press, Cambridge, UK).
6. Hassoun S, McBride T, Russel DR (2000) Developement of perfluorocarbon tracer technology for underground leak location. *J Environ Monitor* 2:432–435.
7. Spence RK (1995) Perfluorocarbons in the twenty-first century: Clinical applications as transfusion alternatives. *Artif Cell Blood Sub* 23:367–380.
8. Bera PP, Francisco JS, Lee TJ (2009) Identifying the molecular origin of global warming. *J Phys Chem A* 113:12694–12699.
9. Hammitt JK, Jain AK, Adams JL, Wuebbles DJ (1996) A welfare-based index for assessing environmental effects of greenhouse-gas emissions. *Nature* 381:301–303.
10. Blowers P, Moline DM, Tetrault KF, Wheeler RR, Tuchawena SL (2008) Global warming potentials of hydrofluoroethers. *Environ Sci Technol* 42:1301–1307.
11. Young CJ, Hurley MD, Wallington TJ, Mabury SA (2008) Molecular structure and radiative efficiency of fluorinated ethers: A structure activity relationship. *J Geophys Res* 113:D24301–D24309.
12. Goody RM, Yung YL (1989) *Atmospheric Radiation: Theoretical Basis* (Oxford Univ Press, New York).
13. Kemp DD (1994) *Global Environmental Issues: A Climatological Approach* (Routledge, London).
14. Wallington TJ, Hurley MD, Nielsen OJ (2009) The radiative efficeincy of HCF2OCF2OCF2CF2OCF2H (h-galden 1040x) revisited. *Atmos Environ* 43:4247–4249.
15. Blowers P, Moline DM, Tetrault KF, Wheeler RR, Tetrault KF (2007) Prediction of radiative forcing values for hydrofluoroethers using density functional theory methods. *J Geophys Res* 112:D15108–D15126.
16. Dunning TH (1970) Gaussian basis functions for use in molecular calculations. I. Contraction of (9s5p) atomic basis sets for the first-row atoms. *J Chem Phys* 53:2823–2833.
17. Dunning TH (1971) Gaussian basis functions for use in molecular calculations. IV. The representation of polarization functions for the first row atoms and hydrogen. *J Chem Phys* 55:3958–3966.
18. Lee TJ, Schaefer HF (1985) Systematic study of molecular anions within the self-consistent field approximation: OH-, CN-, C2H-, NH2- and CH3-. *J Chem Phys* 83:1784–1794.
19. Shao Y, et al. (2006) Advances in methods and algorithms in a modern quantum chemistry program package. *Phys Chem Chem Phys* 8:3172–3191.
20. Wilson EBJ, Decius JC, CP P (1980) *Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra* (Dover, New York).
21. Galabov B, Yamaguchi Y, Remington RB, Schaefer HF (2002) High level ab initio quantum mechanical predictions of infrared intensities. *J Phys Chem A* 106:819–832.

*Intder2005 is a general program written by W. D. Allen and co-workers, which performs vibrational analysis and higher-order nonlinear transformations.